

UDC 666.175.6

DEVELOPMENT OF COMPOSITIONS AND PRODUCTION TECHNOLOGY FOR ELECTROVACUUM TINTED GLASS

I. M. Tereshchenko,¹ É. A. Kuzina,¹ and R. Yu. Popov¹

Translated from Steklo i Keramika, No. 6, pp. 19–21, June, 2005.

The possibility of tinting industrial glasses with cadmium sulfoselenides is discussed. Glass compositions for making car headlights and their tinting technology are proposed. The melting and molding parameters for such lamp bulbs are identified. Experimental samples of yellow glass bulbs are obtained.

The Brest Elastic Lamp Works JSC is one of the leading companies in the CIS producing a wide range of incandescent lamps for general and special purposes used in various sectors of industry, in illuminating civic buildings, and in transport vehicles. The company currently produces 36 types of automobile lamps used for illumination and signals in road equipment and vehicles. However, the present economic situation calls for renewing the product range and searching for new market niches. Among promising products one could include lamps with tinted glass bulbs that are extensively used in new design of automobile headlight and lighting systems, for instance PY21W lamps with a yellow glass bulb. The colorimetric and optical parameters of such glass should meet the following requirements of the MKO standard: light transmission over 65%, dominant wavelength 580 nm, and color frequency over 80%.

At the first stage of the research, the researchers from the Department of Glass and Ceramic Technology at the Belarus Technological University and the technologists of the Brest Electric Lamp Works had to identify the type of colorants and glass compositions that could provide the specified parameters.

The study of the transmission spectra and optical parameters of synthesized glasses tinted with carbon, sulfur, selenium, and cadmium sulfide indicated that only glasses tinted with cadmium sulfoselenides provide the required colorimetric and optical parameters of glasses and can be regulated within wide limits. Such glasses can be clear in melting, and a desired color shade can be “induced” in molding or in the course of special thermal treatment.

At the second stage, we investigated the possibility of tinting clean glass by cadmium sulfoselenides in the work flow (in the feeder), which is a novel technique in the pro-

duction of electrovacuum glass. The method implies using a feeder with a conversion chamber, to which colorant mixtures (pigment + low-melting component) are fed. The clear glass melt flow at a temperature of 1250–1300°C is mixed with the colorant by a mixer. The specific feature of this glass-tinting technique is the possibility of a rapid transition from one color to another and back [1]. The experiments were conducted in laboratory conditions, simulating the conditions of the feeder converter in a heated crucible. The glass selected for tinting was electrovacuum glass SL-96 used at the Brest Electric Lamp Works to produce clear glass bulbs, which could allow the company to produce clear and tinted glass melt in the same furnace. The low-melting component in the colorant mixtures was represented by up to 4% (here and elsewhere wt.%) NaF and Na₂SiO₃ (above 100%) with the pigment content equal to 0.1–0.5% Se and 0.7–1.8% CdS. The following results were obtained:

- intense burning and evaporation of pigments, especially of selenium, is observed at the moment of their contact with the hot glass melt;
- insufficiently uniform distribution of the colorant in the glass melt due to the increased viscosity of the latter;
- colorant complexes responsible for the red tint (CdSe) have no time to be formed under the specified experimental conditions.

Glass tinting varied from yellow-brown to intense brown depending on the concentration of the colorant introduced. As a consequence, the color purity of the resulting samples did not exceed 55–60%. The dominant wavelength was 568–572 nm, the transmission spectra of the experimental glasses tinted in the work flow exhibited a gradual smooth rise of the transmission limit (Fig. 1, composition 5).

Thus, the attempt to tint industrially produced electrovacuum glass SL-96 by cadmium sulfoselenides in the work flow produced negative results and afterwards we considered

¹ Belarus State Technological University, Minsk, Belarus; Brest Electric Lamp Works Joint-Stock Company, Brest, Belarus.

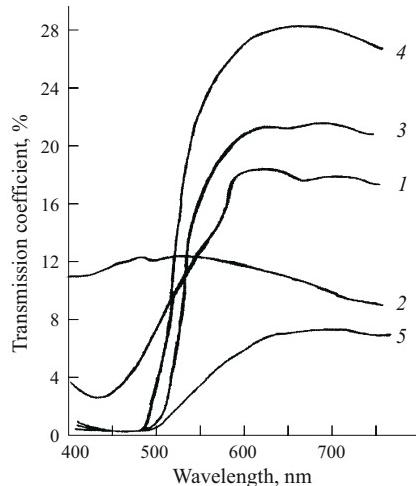


Fig. 1. Transmission spectra of experimental glasses in visible spectrum range (sample thickness 6 mm): 1, 2, 3, 4, and 5) CdS + Se content equal to 1.2 + 0.4, 1.0 + 0.5, 0.5 + 0.2, 2.0 + 0.0, and 0.8 + 0.6%, respectively.

only the method of introducing colorants directly into the batch. In such a case, the company ought to have a separated tank furnace of low capacity (around 4 tons/day), which correlates with the output of the tinted bulb production line. Since tinting with cadmium sulfoselenides requires the presence of certain oxides in the glass composition (K_2O , B_2O_3 , ZnO) [2], it was decided to produce experimental glass compositions in the $SiO_2 - CaO - ZnO - Na_2O - K_2O$ system with Al_2O_3 and B_2O_3 additives, resembling glass SL-96 in their main properties. The content of SiO_2 varied in the limits of 62 – 71%, ZnO from 0 to 9%, CaO from 1 to 10%, and the content of alkali oxides was 16 – 17%. Glasses were melted in porcelain crucibles in a gas furnace at a temperature of 1400°C with 1-h exposure at the maximum temperature. Altogether 28 compositions were prepared. They were used to study their crystallization capacity, softening temperature, CLTE, chemical resistance, transmission spectra, and chromaticity.

The data of the thermal analysis and mass crystallization of glasses (up to 1000°C) were used to determine the range of compositions resistant to crystallization. The thermograms of such glasses exhibit an endothermic effect related to the modification of the structure in the transition from a brittle state to the plastic state and sometimes a slight effect in the range of 960 – 1000°C accompanied by the opacification of glass caused by the crystallization of the colorant complexes of the colloid type (“roasting”) [3].

In subsequent studies we identified the regularities of the variation experimental glass properties depending on their chemical compositions. It was established that the density and CLTE of glasses depend perceptibly on the $CaO : ZnO$ ratio. Based on the experimental glasses, it is possible to obtain a wide range of color shades under a minimum content of ZnO (3%) in the course of its replacement by CaO .

Glasses with a lower content of ZnO after melting were clear. The spectral characteristics of glasses were studied in the wavelength range of 400 – 750 nm. The specific feature of their transmission spectra is a sharp rise in their curves; as a consequence, these glasses had weak light absorption in the red part of the visible spectrum and virtually total absorption in the blue and green spectrum ranges (Fig. 1, compositions 1, 3, and 4).

Glasses with an exceptional color purity exceeding 90% were obtained; therefore their color and transparency varied little with varying glass thickness, which is a significant advantage. Tinting glass with a low ZnO content (below 3%) can be achieved only after additional thermal treatment (inducing) at 520 – 560°C. In this case the variation of the glass tint from light green to ruby is related to the modification of the ratio between the color complexes CdS and $CdSe$ in glass. Based on the studies performed, the optimum glass composition 2-op was selected, which was tested in the industry. The specified composition has a high content of alkali (17%) and alkaline-earth (10%) components; the content of B_2O_3 content is 3% and the (Se + CdS) content is 1.2%.

The experimental composition was melted in an industrial pot furnace in a pot of capacity 300 liters under the following conditions. Industrial glass (selenium ruby) cullet (around 60 kg) was introduced at 1360°C and covered the batch to avoid the entrainment of volatile components. The atmosphere in the furnace was maintained strictly neutral. The batch was fed into the pot in large portions at the melting temperature of 1340°C; in working glass the temperature in the furnace was lowered to 1140°C. Experimental glass was partly formed in metallic molds or extruded in the form of a tube of length 4 – 8 m (manual molding). When molded in metal molds, the tint of the samples varied from clear to a slightly yellow shade depending on the cooling rate. This is evidence that the glass melt at high temperatures is clear and the color is “induced” either in working or in subsequent thermal treatment. Depending on the glass melt cooling rate, it is possible in molding to obtain a wide range of color shades: from light green to yellow, orange, and ruby.

The content of the colorant components (CdS and Se) in the glass melt exceeded the prescribed values due to the use of industrial ruby glass cullet, which has an increased content of these pigments. As a consequence, the red color dominated in tubes extruded from glass 2-op. In general the final color of the product in manual forming depends on the heating duration of the glass melt portion and the subsequent extrusion velocity. The following regularity was observed: the longer the heating duration and the slower the extruding velocity, the more intense is the color of the product and the greater is the dominance of red hues. The capacity of the specified glass for extruding tubes was estimated as excellent. This is due to the substantial “length” of glass and the presence of sulfur in its composition, which raises the elasticity of the glass melt. Altogether 80 m of tubes of a preset diameter (about 14 mm) were extruded with a wall thickness of about 1 mm.

The following characteristics feature of experimental glasses is worth noting: the treatment of molded tinted products using a gas burner with an oxidizing flame does not change its tint "induced" in molding. Only a highly reducing flame produces a shift in the color tone toward the red spectrum range. Color stability under subsequent heat treatment is an important factor for the production of automobile lamps, where tinted glass bulbs are subjected to additional thermal treatment [2].

However, a tint can be induced in experimental glasses under a sufficiently long exposure (20–30 min) in an electric furnace at a temperature of 560–640°C. In the laboratory conditions, a color was "induced" in samples of glass 2-op produced by casting in metallic molds. Depending on temperature and exposure duration, the color of glass varied from light yellow to ruby passing via all intermediate shades. This makes it possible to control the tinting of products molded from glass 2-op. The dilatometric curve of glass 2-op is shown in Fig. 2.

Lamp bulbs are produced in the glass division of the Brest Electric Lamp Works. Tinted glass tubes produced earlier are cut into preforms of length about 1 nm; next, bulbs ShK-26 are blown on semiautomatic machines BZ 12-01. The cupola part of the bulb has a typical defect known as a "decolorized lens" in the form of a glass drop formed in the course of automatic blowing of the bulb during the cutting and sealing of the tube end using an oxygen burner flame. Evidently, under the effect of the flame the temperature in this part of the bulb becomes so high that the colorant is partly burned out. Attempts to eliminate this defect were unsuccessful. Accordingly, despite the fact that inducing color for 30 min at 560°C imparts a homogenous tint to the pro-

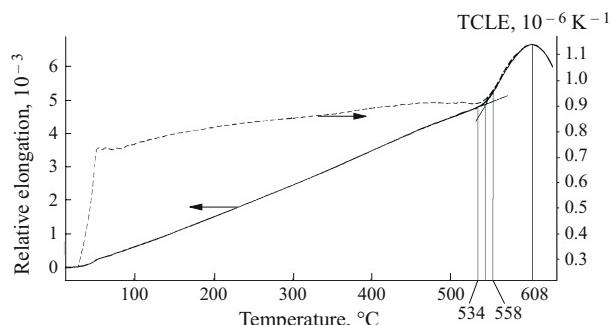


Fig. 2. Dilatometric curves of optimum glass composition 2-op.

duct, it was concluded that bulbs have to be formed on Olivotto machines from bulk-tinted glass.

We also verified the suitability of tinted glass for manual glass blowing in metallic molds. An optimum glass portion was selected to produce a ShK-26 bulb (diameter 26 mm, height 57 mm) and its uniform distribution in the mold was achieved, with the wall thickness in the bulb sphere equal to 0.5–0.6 mm, in the bulb neck equal to 0.9–1.0 mm, and the wall thickness deviations below 0.1 mm, which provides for efficient bulb-assembly technology.

REFERENCES

1. "Tinting glass melt in a feeder," *Steklo Mira*, No. 4, 55–58 (2001).
2. A. N. Dauval'ter, *Crystal, Tinted, and Opal Glasses* [in Russian], Gizlegprom, Moscow (1957).
3. I. I. Kotsik, N. P. Nebrezhskii, and I. O. Fanderlik, *Tinting of Glass* [in Russian], Stroizdat, Moscow (1983).